Efficient conversion of levulinic acid into alkyl levulinates catalyzed by sulfonic mesostructured silicas

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Published on:
Applied Catalysis A: General 466 (2013) 116–122
http://dx.doi.org/10.1016/j.apcata.2013.06.035
ABSTRACT

Sulfonic mesoporous silicas have demonstrated an outstanding catalytic performance in the esterification of levulinic acid with different alcohols to produce alkyl levulinates, a family of chemicals considered to be excellent oxygenated fuel extenders for gasoline, diesel and biodiesel. Catalyst screening indicated that propylsulfonic acid-modified SBA-15 material was the most active one, among tested materials, due to a combination of moderately strong sulfonic acid sites with relative high surface hydrophobicity. Under optimized reaction conditions (T = 117 °C, ethanol/levulinic acid molar ratio = 4.86/1 and catalyst/levulinic acid = 7 wt.% ) almost 100% of levulinic acid conversion was achieved after 2 h of reaction, being negligible the presence of levulinic acid by-products or ethers coming from intermolecular dehydration of alcohols. The catalyst has been reused, without any regeneration treatment, up to three times keeping almost the high initial activity. Interestingly, a close catalytic performance to that achieved using ethanol has been obtained with bulkier alcohols.

Keywords: sulfonic acids, levulinic acid, alkyl levulinates, fuel formulation, acid catalysis.

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1. INTRODUCTION

The transport sector represents around 30% of total world consumed energy and this percentage reaches a still higher level for the EU members states (ca. 33%). Currently, the transportation fuel sector predominantly depends on a single non-renewable source of energy, namely petroleum (ca. 96%). Consequently, this sector is highly vulnerable to oscillations in oil market and responsible for high greenhouse gas emissions. In order to smooth this situation, the EU has defined an ambitious plan in which “each member state shall ensure that the share of energy from renewable sources in all forms of transport in 2020 is at least 10% of the final consumption of energy in transport in that member state” [1]. Carbon-based biofuels serves as a promising short- and medium-term alternative to petroleum-derived fuels. These biofuels can be derived from renewable carbon sources to mitigate greenhouse emissions. The applicability of biomass as renewable carbon sources for transportation fuels has been demonstrated by the successful integration of first generation bioethanol and biodiesel into the current infrastructure, and their application has facilitated a reduced dependence from fossil fuels. However, first generation biofuels production technologies use easy accessible edible biomass, thereby impacting the supply of food for humans and animals. Furthermore, their availability is not sufficient to satisfy the demands presently met by petroleum. Likewise, their extensive and continued production is not a sustainable solution. Moreover, European Commission has recently published a proposal to limit global land conversion for biofuel production, and raise the climate benefits of biofuels used in the EU (Brussels, October 17th, 2012). The use of food-based biofuels to meet the 10% renewable energy target of the Renewable Energy Directive will be limited to 5%. This is to stimulate the development of alternative, so-called second generation biofuels, from non-food feedstock, like waste or straw, which emit substantially less greenhouse gases than fossil fuels and do not directly interfere with global food production.

These important limitations of conventional biofuels (first generation) and new trends in legislation have stimulated the research for new technologies that allow high energy-density, infrastructure-compatible fuels (advanced biofuels) which could be easily implemented in the existing hydrocarbon-based transportation infrastructure (eg. engines, fuelling stations, distribution networks and petrochemical processes) and using lignocellulose as raw material which is widely available (as waste biomass, conventional wood, and fast rotation crops) instead of edible biomass. Among the different advanced biofuels not using edible biomass as raw material, alkyl levulinates have been proposed as excellent candidates for the formulation of gasoline, diesel and biodiesel [2-8].
Up to now, there are four developed potential pathways for the synthesis of levulinate esters from cellulosic biomass (Fig. 1). Levulinates can be directly obtained from C₆ carbohydrate-based biomass, i.e. fructose, glucose, sucrose, cellulose and the like, in alcoholic medium, without the need of first isolating levulinic acid (route a, Fig. 1). This approach has been addressed in presence of acid homogeneous and heterogeneous catalysts [9-14]. Aside from the direct production of alkyl levulinates, the use of an alcoholic medium for the treatment of lignocellulosic biomass has also the added advantage of minimizing the formation of undesired by-products, since polymeric humin formation greatly diminishes levulinic acid yields in acid treatment of C₆ sugars in aqueous medium [15]. However this approach shows serious drawbacks limiting its application beyond the bench scale [16]: reduced yields towards levulinates (on the order of 20%); the intermolecular dehydration of alcohols is observed in significant extent; limited recyclability of the catalysts; high required temperatures especially for dealing with polymeric feedstock; and finally works reported in literature have just focused on the use of low molecular weight alcohols (methanol or ethanol), so that their validity is not assessed for bulkier alcohols. In other approach, levulinates can be obtained by alcoholysis of 5-(chloro-methyl) furfural (CMF; route b, Fig. 1). CMF can be obtained from chemical digestion of sugars, cellulose and lignocellulosic feedstock with hydrochloric acid in a biphasic reactor with product yields in the range of 80-95% [17]. Further reaction of isolated CMF in the presence of alcohols gives the corresponding levulinates with yields around 80%. Although a high levulinate yield is obtained using this approach, there are still some concerns about the recycle of HCl and the waste disposal problems. Other route is the production of alkyl levulinates by alcoholysis of furfuryl alcohol obtained from hydrogenation of biomass-derived furfural (route c, Fig. 1). The furfural hydrogenation step is carried out using Cu-based catalysts, whereas the subsequent alcoholysis has been addressed with acid catalysts such as strong homogenous acids, polymeric resins and zeolites [18-19]. The profitability potential of this approach is limited for the high formation of ether by-products during the alcoholysis step [18-19].

Finally, alkyl levulinates can be prepared by the esterification of levulinic acid in the presence of alcohols under moderate temperatures (route d, Fig. 1). This approach should then be based in an efficient production of levulinic acid. In this context, although several routes have been described in literature for levulinic acid production, the highest yields from biomass are so far claimed by the commercial “Biofine” process, a two-stage process with yields in the range 70-80% [20-21]. Once the levulinic acid has been obtained, its reaction with primary alcohols, such as ethanol, occurs even at room temperature, but the reaction is very slow and needs to be accelerated either by using high temperature or a catalyst to achieve the equilibrium conversion in a reasonable period of time. Thus, levulinic acid esters can be obtained by
esterification reaction in the presence of a homogeneous acid catalyst, such as sulfuric and p-toluenesulfonic acid. However, the use of solid (heterogeneous) acid catalysts is more desirable because solids are easier to recover and reuse, there is no need for neutralization, and corrosion associated to their use is limited in comparison to mineral acids. In literature, many solid acids have been proposed for several esterification reactions, but for this particular system the number of studies is still very limited. Thus, Dharne et al. [22] have synthesized n-butyl levulinate by esterification of levulinic acid with n-butanol using heteropolyacids supported over acid-treated clay montmorillonite reaching acid conversions up to 97% and 100% selectivity towards the levulinate. Nevertheless, the catalyst showed a poor reusability. Pasquale et al. have incorporated Wells-Dawson heteropolyacid structures in a silica framework by the sol-gel technique and have shown that the resultant acid catalysts are active and selective in the esterification of levulinic acid with ethanol [23]. Yan et al. have also recently obtained good catalytic activity for the production of methyl and ethyl levulinates over mesoporous H_{2}SiW_{12}O_{40}-SiO_{2} catalysts (73% yield of methyl levulinate and 67% yield of ethyl levulinate) but using a large excess of catalyst [24]. Finally, Fernandes et al. have evaluated and compared the activities of different zeolites (HUSY, HBEA, HMOR, HZSM-5, HMCMS-22) and sulfated oxides (SnO_{2}, ZrO_{2}, Nb_{2}O_{5}, TiO_{2}) to that presented by a commercial sulfonic resin (Amberlyst-15) in the esterification of levulinic acid with ethanol [25]. They found that while there is a correlation between the number of acidic sites and the activity for the sulfated oxides, the same is not true for the studied zeolites where the narrow pore channels play a more important role. Among the tested catalysts, Amberlyst-15 and sulfated SnO_{2} showed a remarkable high yield of ethyl levulinate, probably due to the strong acidity provided by -SO_{3}H functional groups and SO_{4}^{2-} species, respectively. However, sulfate groups in SO_{4}^{2-}/SnO_{2} catalyst undergo significant leaching/solubilization into reaction medium, which discards this catalyst as adequate. It is interesting to note that in these works the intermolecular dehydration of alcohols was not observed. Hence, since levulinic acid can be commercially obtained from lignocellulosic biomass, its esterification with alcohols under moderate reaction conditions can be considered as an attractive alternative to produce alkyl levulinates.

Organosulfonic acid-modified mesoporous materials with strong acidity, high specific surface area and well ordered mesoporosity are able to carry out different acid-catalyzed reactions in the processing of bulky substrates and attaining high conversions and selectivities. Within the scope of this work, the esterification of levulinic acid with different alcohols has been studied over this kind of organically modified silicas. Firstly, the catalytic performance of this type of catalysts has been benchmarked with other sulfonic acid-containing commercial catalysts in the esterification of levulinic acid with ethanol. Following, a multivariable analysis has been used to assess the conditions (ethanol/levulinic acid molar ratio and temperature) that
yield the best catalytic results in terms of levulinic acid conversion and yield towards the ethyl levulinate over this catalyst. Finally, the catalytic performance under the optimized reaction conditions was assessed in the esterification of levulinic acid using other non ethanol alcohols (methanol, iso-propanol and 2-butanol). The reusability of the catalyst after several reaction cycles has also been evaluated.

2. EXPERIMENTAL

2.1 Catalysts

*Propylsulfonic-acid functionalized mesostructured silica* (Pr-SO$_3$H-SBA-15) was synthesized following a previously reported procedure [26]. Molar composition of the synthesis mixture for 4 g of template block-copolymer (Pluronic 123, EO$_{20}$PO$_{70}$EO$_{20}$, Sigma-Aldrich) was: 0.0369 tetraethylorthosilicate (TEOS, Sigma-Aldrich); 0.0041 mercaptopropyltrimethoxysilane (MPTMS, Sigma-Aldrich); 0.0369 H$_2$O$_2$; 0.24 HCl; $\approx$ 6.67 H$_2$O. *Arenesulfonic-acid functionalized mesostructured silica* (Ar-SO$_3$H-SBA-15) was synthesized as described elsewhere [27]. For this catalyst, the molar composition of the synthesis mixture for 4 g of copolymer was as follows: 0.0369 TEOS; 0.0041 chlorosulfonyl-phenylethyltrimethoxysilane (CSPTMS, Gelest); 0.24 HCl; $\approx$ 6.67 H$_2$O. In both cases, the amounts of sulfur precursors (MPTMS and CSPTMS) have been selected to provide 10% of total silicon moles. These two sulfonic acid-modified mesostructured silicas provide different acid strengths, as introduced by the different molecular environments of the sulfonic acid sites (Pr-SO$_3$H-SBA-15 < Ar-SO$_3$H-SBA-15).

Different commercial acid catalysts were also evaluated in this work. Acidic macroporous resins such as Amberlyst 15 (Romh & Haas) and NR-50 (super-acidic perfluorinated resin-sulfonic catalyst, DuPont), as well as SAC-13 Nafion®-SiO$_2$ composite (fluorosulfonic acid Nafion® polymer on amorphous silica with resin content in the range of 10-20 wt.%, DuPont); were supplied by Sigma-Aldrich. Sulfonic modified amorphous silicas functionalized with propyl- and arene-sulfonic moieties were provided by Silicycle (Pr-SO$_3$H-SiO$_2$ and Ar-SO$_3$H-SiO$_2$). *p*-Toluenesulfonic acid (*p*-TSA) was selected as homogeneous reference catalyst.

2.2 Characterization

Textural properties of sulfonic acid-modified mesostructured silicas have been assessed by means of nitrogen adsorption and desorption isotherm at 77 K using a Micromeritics TRISTAR.
Pores sizes distributions were calculated using the BJH method using the KJS correction, and total pore volume was taken at P/P₀ = 0.975 single point. Structural characterization was completed by X-ray powder diffraction (XRD) patterns, which were acquired on a PHILIPS X’PERT diffractometer using Cu Kα radiation. Data were recorded from 0.6 to 5° (2θ) using a 0.02° step resolution. Acid capacity was measured through the determination of cationic-exchange capacity using sodium as cationic-exchange agent [26-27]. In a typical experiment, 0.05 g of solid was added to 10 g of 2M NaCl (aq.), and the resultant suspension was allowed to equilibrate and thereafter titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq). Estimated error is in the range ±0.05 meqH⁺/g. Thermogravimetric analyses (TGA) were performed in a SDT 2960 Simultaneous DSC-TGA, from TA Instruments with an air flow rate of 100 mL/min and a heating ramp of 5°C/min.

Table 1 summarizes the most relevant physicochemical properties for the two sulfonic acid-modified mesostructured silicas. Data from XRD and N₂ adsorption isotherms evidence high mesoscopic ordering and high surface areas along with narrow pores sizes distributions around 8-9 nm (size enough to avoid the steric constraints imposed by pore size when processing relatively bulky substrates such as derived levulinates). Additionally, for comparison purposes, some characterization data corresponding to the commercial sulfonic modified catalysts used in this study is summarized in Table 2. In this case, characterization is mainly provided by the commercial suppliers.

2.3 Catalytic tests procedure

Catalyst screening in the esterification of levulinic acid (LA, Sigma Aldrich) with ethanol (EtOH, Scharlab) was accomplished in a round bottom flask fitted with a reflux condenser. Typically, levulinic acid and ethanol were loaded together into the flask followed by the addition of the corresponding catalyst. The weight of the dried catalysts was calculated with the purpose of keeping constant the acid sites concentration in the reaction medium according to acid capacities depicted in Tables 1 and 2 (0.072 mmol of H⁺ per gram of levulinic acid; the initial amount of levulinic acid was 7 g). The catalytic tests were performed at 343 K for 3 hours using excess of ethanol (EtOH/LA molar ratio = 5/1). Reaction aliquots were periodically withdrawn and filtered prior to their analysis by gas chromatography (see below).

Esterification experiments for the multivariate analysis were performed in liquid phase at temperatures ranging from 70 to 130 °C in a stainless steel stirred autoclave (25 mL) equipped with a temperature controller and a pressure gauge. Once the reactants and catalysts were fed to
the reactor, the temperature was raised to the desired value. Pressure conditions were those corresponding to the autogenous pressure. Stirring was fixed for all the experiments at 1000 rpm to avoid external diffusional limitations and the reaction time was set at 2 hours. EtOH/LA molar ratio (MR) ranged from 2.5/1 to 7.5/1 and a constant catalyst loading of 7 wt.% (referred to initial mass of levulinic acid) was used. The screening of the different alcohols was carried out under the optimized reaction conditions derived from the multivariate analysis. Reusability of the catalyst was evaluated under the optimized reaction conditions in four consecutive catalytic runs. After each catalytic cycle, the catalyst was recovered by filtration, thoroughly washed with acetone at room temperature and dried overnight at 110 °C before being reused again under the same reaction conditions.

2.4 Product analysis

Reaction samples were analyzed by GC (Varian 3900 gas chromatograph) using a ZB-WAX Plus column (30 m x 0.53 mm, DF=1.00 µm) and a FID detector. Reaction products detected by GC included levulinic acid and alky levulinates but ethers coming from the intermolecular dehydration of alcohols, or other by-products were not observed under the relatively moderate reaction conditions tested in this work. The quantification of the levulinic acid was obtained using commercial LA to calculate the corresponding response factor. Catalytic results are shown in terms of absolute conversion of levulinic acid (that in this case equals the alkyl levulinate yield). Calculus of levulinic acid conversion was performed based on the chromatographic quantification of the levulinic acid remaining after the reaction using the following equation:

\[
X_{LA} = \frac{(\text{starting mmol of levulinic acid}) - (\text{final mmol of levulinic acid})}{\text{starting mmol of levulinic acid}} \times 100
\]

3. RESULTS AND DISCUSSION

3.1 Screening of sulfonic acid-modified catalysts

The feasibility of tuning the acid strength of the sulfonic acid groups by close attachment of different moieties has led before to improvements in their catalytic activity in several acid-catalyzed reactions [28]. In this work, the catalytic performances of three different types of sulfonic acid sites, i.e. propyl-, arene- and fluoro-sulfonic acid sites, have been analyzed in the esterification of levulinic acid with ethanol. The different nature of the molecular environment
of the SO$_3$H sites defines their acid strength. Thus, highly electronegative fluorine atoms provide higher acid strength than an aromatic ring, such as in arene-sulfonic acid centres, which in turn gives stronger acid sites than alkyl moieties like those in the propyl-sulfonic acid-modified catalysts. Taking this into account, the synthesized propyl- and arene- sulfonic acid-modified SBA-15 catalysts have been benchmarked with other sulfonic acid-based commercial solid catalysts conventionally used in acid catalyzed processes. Selected comparative catalysts include Amberlyst-15, a cationic-exchange resin based in arenesulfonic acid groups, with an acid strength similar to that of Ar-SO$_3$H-SBA-15 [27]; two Nafion catalysts, the resin NR-50 and the silica composite SAC-13, both based on strong fluorosulfonic acid sites; and two amorphous non-structured silicas, Pr-SO$_3$H-SiO2 and Ar-SO$_3$H-SiO2, with grafted propyl- and arene-sulfonic acid groups, respectively. Two reaction tests, one of them blank reaction (performed in absence of catalyst) and another one carried out with a homogenous catalyst (p-toluene sulfonic acid), have also been included as references for comparison purposes. Reaction conditions selected for this preliminary screening were those reported by Fernandes et al. [25] (70 ºC reaction temperature and 5/1 EtOH/LA molar ratio) but keeping constant the concentration of sulfonic sites in the reaction medium with the aim to elucidate the true influence of the different sulfonic site environments on the catalytic performance. The results of LA esterification with ethanol in all these experiments are depicted in Fig. 2.

Blank reaction experiment, in the absence of catalyst, gave a LA conversion of ca. 5% after 3 hours of reaction indicating that, under the tested reaction conditions, the extent of the esterification of levulinic acid by auto catalysis is negligible. This result can be considered as the minimum LA conversion to be achieved on each experiment. In contrast, all the catalysts tested in this work resulted in higher product yields than that corresponding to the blank reaction reference, evidencing the necessity of an acid catalyst, at least stronger than levulinic acid, to carry out this reaction. Highest LA conversion values were obtained over the homogeneous catalyst (p-toluene sulfonic acid). In this case, the complete absence of diffusional limitations makes it the most active catalyst. Nevertheless, despite its remarkable catalytic performance, liquid acids still present the operational and environmental drawbacks generally attributed to homogeneous catalysis. Interestingly, sulfonic acid-modified mesostructured catalyst showed outstanding catalytic activities as compared to the rest of solid catalysts, and close to the homogeneous acid, evidencing the high accessibility of the SO$_3$H sites and low diffusional limitations in mesostructured SBA-15 silica. Likewise, despite their lower intrinsic acid strengths, propyl-SO$_3$H acid sites gave higher catalytic activities than arene-SO$_3$H groups. A feasible explanation for this behaviour is that more hydrophobic local environments near the propyl-sulfonic acid sites result in reduced poisoning by adsorbed water, which is formed during the reaction [29-30]. In order to validate the effect of the silica mesostructure, propyl-
and arene-SO₂H-functionalized non-ordered amorphous silicas were evaluated. As shown in Fig. 2, the lower LA conversion over these catalysts confirms that the presence of a highly ordered mesostructured support with high surface area (as in SBA-15 materials) improves the catalytic activity of the SO₃H groups, either because of the existence of lower mass transfer limitations or because of a higher accessibility to the catalytic acid sites.

Commercially available sulfonated-resin-based catalysts (Amberlyst-15 and NR-50) are industrially used in different acid-catalyzed processes. However, in the present study of esterification of levulinic acid these have provided very low conversion values. Low surface areas and their highly hygroscopic nature are the main causes attributed to their poor activity. Both types of sulfonic acid resins (sulfonated polystyrene in the case of Amberlyst and fluorinated alkyl-SO₂H chains in the case of Nafion NR-50) present higher acid-strengths and density of acid sites than sulfonated SBA-15 materials. Therefore, the above discussed hydrophilicity detrimental effect for arene-SO₃H SBA-15 is observed over these polymer-based catalysts with an increased intensity. Likewise, the low surface area limits the accessibility of acid sites. In fact, the dispersion of fluorinated alkyl-SO₂H chains over a silica support (SAC-13 catalyst) allowed a significant enhancement of the LA conversion but it is still lower than those of sulfonic modified SBA-15 catalysts. Summarising, propyl-sulfonic acid-modified SBA-15 material, with a moderate density and acid strength of sulfonic acid sites, is shown as an interesting acid catalyst for the esterification of levulinic acid with ethanol.

3.2 Design of experiments

In this part of the work, the production of alkyl levulimates using a propyl-SO₃H-functionalized mesostructured silica (Pr-SO₃H-SBA-15) as catalyst was developed and optimized by following factorial design and response surface methodology [31]. The experimental design applied to this study was a full 2³ design (two factors, each one at three levels). The central point experiment was repeated four times in order to determine the variability of the results and assess the experimental errors. The selected response was the levulinic acid conversion (equivalent to alkyl levulinate yield), Xₖₖ. In this sense, the optimization was carried out to achieve high conversions of levulinic acid. Selection of the factors was based on the operating conditions that have a significant influence on the acid esterification. Chosen factors were temperature, T, and the molar ratio of ethanol to levulinic acid, MR. Selection of the levels was based on results obtained in previous studies [22-25]. The lower and upper temperature levels were 70 and 130°C, respectively. The levels of the EtOH/LA molar ratio were 2.5/1 and 7.5/1 (upper levels were not considered in order to avoid possible intermolecular dehydration of ethanol to produce diethyl ether). Thus, the standard
experimental matrix for the design is shown in Table 3. Fourth and fifth columns represent the 0 and ±1 encoded factor levels on a dimensionless scale, whereas second and third columns represent the factor levels on a natural scale. Experiments were run at random to minimize errors due to possible bias in the variables. Table 3 also shows the LA conversion after 2 hours of reaction.

From the matrix generated by the experimental data and assuming a second-order polynomial model, Equation 1 was obtained by multiple regression analysis. The statistical model is obtained from encoded levels giving the real influence of each variable on the process, and therefore the discussion is made using this model (Eq. 1).

\[ X_{LA} = 95.000 + 21.583 I_T - 5.345 I_{MR} - 18.752 I_T^2 + 8.250 I_{MR} I_T - 6.097 I_{MR}^2 \quad (r^2=0.963) \] (Eq.1)

Statistical analysis of the studied experimental range identifies the temperature as the most important factor in the LA conversion response, having a positive effect on the LA conversion. An enhancement of the temperature produces an increase in the conversion of LA independently of the EtOH/LA molar ratio. In contrast, the alcohol to acid molar ratio affects negatively the LA conversion, though this effect can be considered negligible at high temperatures. In addition, the quadratic effects of both variables have a significant negative influence on the LA conversion. This, in turn, indicates that the increase in the operating variables does not produce a constant rise in the LA conversion, because the curvature effect is significant at high values of these variables. Fig. 3 depicts the response surface plot corresponding to Eq.1 and clearly shows the above commented effect of both reaction variables. The gradual increase of the temperature enhances the formation of ethyl levulinate, independently of the EtOH/LA molar ratio, up to a maximum where the reverse reaction is favored. Additionally, a high concentration of ethanol does not promote the formation of ethyl levulinate due to a high dilution of acid sites and levulinic acid that leads to a decrease in the reaction rate, especially at low temperature. Thus, the optimal values which maximize the LA conversion (or the ethyl levulinate yield) under the range of study are an intermediate EtOH/LA molar ratio (4.86/1) and a temperature of 117 ºC. Finally, the arithmetical average and the standard deviation of the LA response were calculated for the central point replicas: \( X_{LA} = 96.05 \pm 3.34\% \). As shown, the standard deviation is lower than 4% and therefore the experimental error is not excessively significant.

Additionally, the stability of the Pr-SO\(_3\)H-SBA-15 catalyst was evaluated in the esterification reaction by performing consecutive batch reactions under the optimized reaction conditions. The LA conversions after three reaction cycles are summarized in Table 4. After the first cycle, the LA conversion slightly decreased but then the catalyst activity was stabilized
during two additional reaction cycles. Pr-SO$_3$H-SBA-15 catalyst was recovered after the third reuse and subjected to characterization. TG analyses (Fig. 4, left) and textural properties (Fig. 4, right) of four-times used and fresh catalyst are very similar, evidencing that the sulfonic sites and the mesoscopic structure were preserved after four reaction cycles. Hence, the slight decrease in the LA conversion after the first catalytic use might be attributed to some deposition of organic compounds over the catalyst surface (see TG analysis for the used catalyst in the range of 100-400 °C) which likely hinders the accessibility of reactants to some sulfonic acid sites. It must also be noted that the catalyst is just washed with acetone at RT after the catalytic test, and this mild treatment would not be effective enough to remove some strongly adsorbed organic species.

3.3 Esterification of levulinic acid over Pr-SO$_3$H-SBA-15 catalyst in the presence of different alcohols.

Aside of current commercial usage in food and other industries, ethyl levulinate can be used as octane booster for gasoline [7] and fuel extender for diesel [8] and biodiesel [9]. However, other higher alkyl levulinates like butyl levulinate are also found to be good quality improvers for diesel and biodiesel [3]. In order to generalize the activity of Pr-SO$_3$H SBA-15 catalyst for the esterification of LA in presence of different alcohols, methanol, iso-propanol and 2-butanol have also been evaluated leading to the formation of the corresponding alkyl levulinates. Figure 5 shows the levulinic acid conversion with reaction time in the presence of different alcohols under optimized reaction conditions. Lower-alkyl levulinates (methyl levulinate and ethyl levulinate) are produced in a high yield during the first 30 minutes of reaction, reaching almost 100% of LA conversion. In contrast, the LA esterification with bulkier alcohols is slower. This can be related to the reaction mechanism. Thus, the esterification reaction of LA with alcohols follows different steps: adsorption of the LA molecule on the Brönsted acid site forming a protonated intermediate, which is subsequently attacked by the nucleophilic oxygen atom in the alcohol for the formation of the corresponding oxonium ion; finally, the proton transfer from this oxonium ion and the loss of a molecule of water yield the ester and the simultaneous regeneration of the acid site. The nucleophilic attack of bulkier alcohols, such as iso-propanol and 2-butanol, is likely more hindered than in the case of methanol and ethanol, simply attending to steric limitations leading to a decrease of the reaction rate. However, good results (over 70% of LA conversion) were obtained after 4 hours of reaction with any of the alcohols under study. These results clearly demonstrate the possibility of producing different alkyl-levulinates in a high yield over propylsulfonic acid-functionalized SBA-15. Additionally, no ethers coming from the intermolecular dehydration of the different alcohols were observed under the tested reaction conditions.
4. CONCLUSIONS

Propyl- and arene-SO₂H-modified mesostructured SBA-15 materials are shown as active catalysts in the esterification of levulinic acid with ethanol. These materials have displayed outstanding catalytic performances as compared with other commercial sulfonic-acid-based homogeneous and heterogeneous acid catalysts for this particular reaction and with a remarked reusability. Despite their lower acid strength, propyl-SO₂H acid sites provided higher activity than arene-SO₂H groups as a consequence of the lower hydrophilicity of the sulfonic-acid site microenvironment of the former, which reduces the poisoning effect by water molecules coming from the esterification reaction. The high activity of propyl-SO₂H SBA-15 has also been extended to the preparation of alkyl levulinates from different alcohols, where lower alcohols showed faster conversion of levulinic acid than higher alcohols (iso-propanol and 2-butanol) due to steric impediments.

ACKNOLEDGEMENTS

Financial support from the Spanish Ministry of Economy and Competitiveness through the project CTQ2011-28216-C02–01 is kindly acknowledged. B. Hernández thanks Spanish Ministry of Economy and Competitiveness for a FPI grant.

REFERENCES

Table 1. Physicochemical, textural and acid-related properties for sulfonic acid-modified mesostructured silicas.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$d_{100}$</th>
<th>Pore size</th>
<th>BET area</th>
<th>Pore volume</th>
<th>Wall thick</th>
<th>Acid capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr-SO$_3$H-SBA-15</td>
<td>111</td>
<td>90</td>
<td>692</td>
<td>1.18</td>
<td>38</td>
<td>1.03</td>
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<tr>
<td>Ar-SO$_3$H-SBA-15</td>
<td>123</td>
<td>104</td>
<td>741</td>
<td>0.97</td>
<td>38</td>
<td>0.92</td>
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</tbody>
</table>

$^a$ $d$ (100) spacing, measured from small-angle X-ray diffraction.
$^b$ Mean pore size ($D_p$) from adsorption branch applying the BJH model.
$^c$ The pore volume ($V_p$) was taken at $P/P_o = 0.975$ single point.
$^d$ Average pore wall thickness calculated by $a_o$-pore size ($a_o = 2 \times d(100) / \sqrt{3}$).
$^e$ Acid capacities defined as milliequivalents of acid centers per gram of catalyst, obtained by titration (meq H$^+$/g).
Table 2. Physicochemical properties for commercial SO$_3$H-based catalysts $^a$.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Acid capacity (meq H$^+$/g)</th>
<th>BET area (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Pore Size (Å)</th>
<th>T limit (ºC)</th>
</tr>
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<tbody>
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<td>Amberlyst-15</td>
<td>4.80</td>
<td>53</td>
<td>0.4</td>
<td>300</td>
<td>120</td>
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<tr>
<td>Nafion NR-50</td>
<td>0.90</td>
<td>&gt;5</td>
<td>-</td>
<td>-</td>
<td>200</td>
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<tr>
<td>Nafion SAC-13</td>
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<td>0.6</td>
<td>&gt;100</td>
<td>200</td>
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<td>Pr-SO$_3$H-SiO$_2$</td>
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<td>301$^b$</td>
<td>0.44$^b$</td>
<td>20-200$^b$</td>
<td>&gt;200</td>
</tr>
<tr>
<td>Ar-SO$_3$H-SiO$_2$</td>
<td>0.78</td>
<td>279$^b$</td>
<td>0.38$^b$</td>
<td>20-200$^b$</td>
<td>&gt;200</td>
</tr>
</tbody>
</table>

$^a$ Properties provided by the suppliers.

$^b$ Properties evaluated by nitrogen adsorption and desorption isotherm at 77 K.
Table 3. Experiment matrix and experimental results for the esterification of levulinic acid with ethanol over propylsulfonic acid-modified mesostructured silica, Pr-SO$_3$H-SBA-15 [Catalyst/LA = 7 wt.%; Reaction time = 2 hours].

<table>
<thead>
<tr>
<th>Run Number</th>
<th>T (°C)</th>
<th>MR</th>
<th>I$_T$</th>
<th>I$_{MR}$</th>
<th>$X_{LA}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>130</td>
<td>7.5/1</td>
<td>+1</td>
<td>+1</td>
<td>89.8</td>
</tr>
<tr>
<td>2</td>
<td>130</td>
<td>2.5/1</td>
<td>+1</td>
<td>-1</td>
<td>91.3</td>
</tr>
<tr>
<td>3</td>
<td>70</td>
<td>7.5/1</td>
<td>-1</td>
<td>+1</td>
<td>33.4</td>
</tr>
<tr>
<td>4</td>
<td>70</td>
<td>2.5/1</td>
<td>-1</td>
<td>-1</td>
<td>66.9</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>5/1</td>
<td>0</td>
<td>0</td>
<td>92.1</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>5/1</td>
<td>0</td>
<td>0</td>
<td>98.6</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>5/1</td>
<td>0</td>
<td>0</td>
<td>99.1</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>5/1</td>
<td>0</td>
<td>0</td>
<td>94.4</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>7.5/1</td>
<td>0</td>
<td>+1</td>
<td>88.9</td>
</tr>
<tr>
<td>10</td>
<td>130</td>
<td>5/1</td>
<td>+1</td>
<td>0</td>
<td>99.2</td>
</tr>
<tr>
<td>11</td>
<td>100</td>
<td>2.5/1</td>
<td>0</td>
<td>-1</td>
<td>87.0</td>
</tr>
<tr>
<td>12</td>
<td>70</td>
<td>5/1</td>
<td>-1</td>
<td>0</td>
<td>51.5</td>
</tr>
</tbody>
</table>

Note: T, temperature; MR, EtOH/LA molar ratio; I, coded value; $X_{LA}$, conversion of levulinic acid as (mmol of converted levulinic acid / mmol of starting levulinic acid) x 100.
Table 4. Stability of the Pr-SO$_3$H-SBA-15 on the esterification of LA with ethanol under optimized reaction conditions. [Catalyst/LA = 7 wt.%; Alcohol/LA molar ratio = 4.86/1; T = 117 °C; Reaction time = 2 hours].

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction</th>
<th>$X_{LA}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>First use</td>
<td>98.30 ± 3.34%</td>
</tr>
<tr>
<td>2</td>
<td>1$^{st}$ Reuse</td>
<td>87.50 ± 3.34%</td>
</tr>
<tr>
<td>3</td>
<td>2$^{nd}$ Reuse</td>
<td>85.10 ± 3.34%</td>
</tr>
<tr>
<td>4</td>
<td>3$^{rd}$ Reuse</td>
<td>86.00 ± 3.34%</td>
</tr>
</tbody>
</table>
Figure captions

Figure 1. Routes for the production of alkyl levulinates from cellulosic biomass.

Figure 2. Levulinic acid conversion with reaction time for all the tested solid catalysts [T = 75 °C; EtOH/LA molar ratio = 5/1; 0.072 mmols of H⁺ per gram of LA].

Figure 3. Response surface and contour plots of LA conversion. [Catalyst: Pr-SO₃H-SBA-15; Catalyst/LA = 7 wt.%; Reaction time = 2 hours].

Figure 4. TGA analysis (left) and nitrogen adsorption-desorption isotherms at 77 K (right) of fresh and four-times used Pr-SO₃H-SBA-15 catalysts.

Figure 5. Evolution of levulinic acid conversion with reaction time in the presence of different alcohols under optimized reaction conditions. [Catalyst = Pr-SO₃H-SBA-15; Catalyst/LA = 7 wt.%; Alcohol/LA molar ratio = 4.86/1; T = 117 °C].
Figure 1. Melero et al.
Figure 2. Melero et al.
Figure 3. Melero et al.
Figure 4. Melero at al.
Figure 5. Melero at al.